

REIMAGINING OF OPTICAL KERR EFFECT SPECTROSCOPY: DEVELOPMENT OF A NEW SPECTROSCOPIC TECHNIQUE

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Multidimensional nonlinear spectroscopic methods are powerful tools to investigate ultrafast vibrational dynamics and coherences. Several techniques that have recently been applied to excited electronic states require three or more ultrashort pulses to measure the nonlinear optical response. The additional beamsplitters, mirrors and optical delay stages in these techniques complicates their application in the extreme ultraviolet and X-ray regime, where reflectance is low except at grazing incidence. Optical Kerr effect spectroscopy is a traditional two-pulse technique to measure the 3rd-order nonlinear optical susceptibility of molecules in their ground electronic state. Ultrafast transient polarization spectroscopy (UTPS) is an extension of this technique to excited electronic states, enabling coupled electronic and nuclear dynamics to be investigated by the 3rd-order nonlinear optical susceptibility. In UTPS, a pump pulse excites a population, then a Kerr gate and probe pulse monitor the 3rd-order nonlinear response of excited-state molecules, as a function of delay between each of the three pulses. Two-photon absorption of femtosecond pump pulses populate the S₁ excited-state of nitrobenzene. We were able to extract a dephasing time that oscillates as function of the time delay after excitation. This dephasing time and supporting theoretical calculation allows for distinguishing between an intersystem crossing conical intersection and an internal conversion conical intersection on the same excited-state potential energy surface.